



METHOD 1631-E: MERCURY LABORATORY ANALYSIS

by Anthony W. Carroll

U.S Environmental Protection Agency
Science and Ecosystems Support Division

Analytical Support Branch

Inorganic Chemistry Section

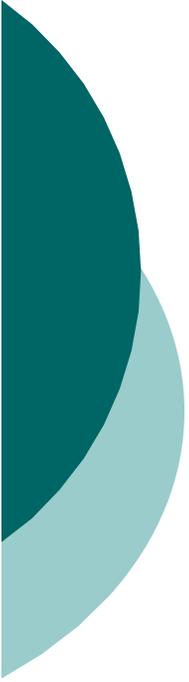
Athens, Georgia

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What is Method 1631E ?

A performance based analytical test method used to determine low level mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry.



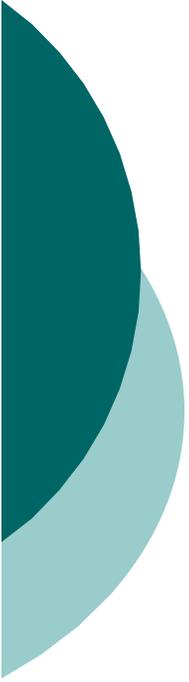
The Evolution of Method 1631

Why was this method needed?

New water quality criteria required lower limits; current limits 1.3 ng/L for wildlife and Method 245.1 reported limits at 200 ng/L.

- **1987**

- **Clean Water Act (CWA)** - Demanded quality-based strategies to ensure that water quality standards were achieved and maintained; included mercury.
- **Great Lakes Initiative- U.S. and Canada** – At the same time, called for the elimination of mercury through pollution reduction.
- **National Toxic Rule**-established maximum concentration limits for mercury and other pollutants.



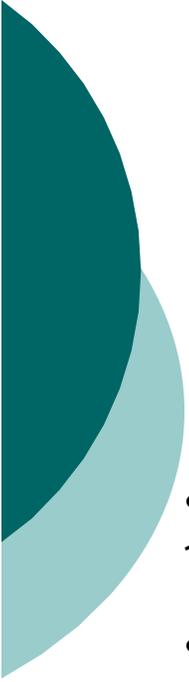
The Evolution of Method 1631

1998 Method 1631-A – Introduced into the CWA; Mercury @ ambient water quality criteria levels – 40 CFR part 136.

1999 Method 1631-B – Included the analysis of effluent matrices.

2001 Method 1631-C

- Clarified method text regarding the reporting and use of field blanks
- Included bubbler blanks or calibration blanks to establish a background for the bubbler system



The Evolution of Method 1631

2001 Method 1631-D – DRAFT

2002 Method 1631- E

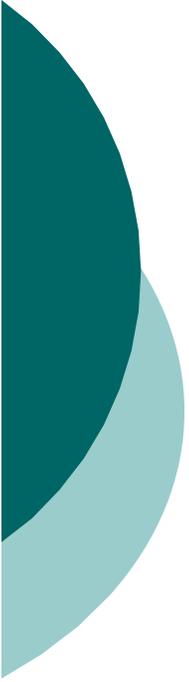
- Allowed the use of automated flow-injection systems (10.3 and 11.2.2).
- Incorporated system blanks for use with automated flow-injection systems (9.4.2 and 10.3.2).
- Defined blank samples (9.4 and 17.0).
- Set requirements for analysis of method blanks (9.4).
- Set frequency for analysis of bottle blanks (6.1.2.4 and 9.4.7).
- Extended calibration range (1.3 and 10.4).
- Removed requirement for immediate sample preservation and refrigeration of unpreserved samples if analyzed within 48 hours; and extended preservation time to 28 days if sample is oxidized in sample container (8.5).



The Evolution of Method 1631

2002 Method 1631- E (cont'd)

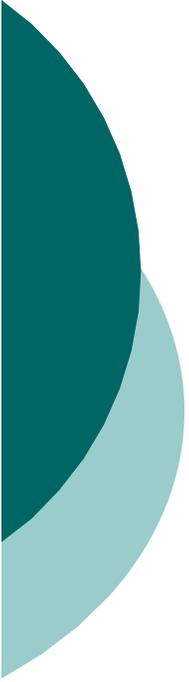
- Extended maximum sample holding time (from collection to analysis) from 28 days to 90days (8.5).
- Incorporated a carryover test (4.2.8.1 and 11.2).
- Allowed shipment of empty bottles for sample collection (6.1.2.1).
- Introduced spike requirements for analytical batches (11.1.2).
- Reemphasized the need to use only glass and fluoropolymer bottles for sample collection (4.3.7 and 8.2).
- Filtration of both field and laboratory samples (2.2 and 8.4).
- Define the limits of performance requirements (6.1.3.2 and 6.1.3.3).



Method Differences

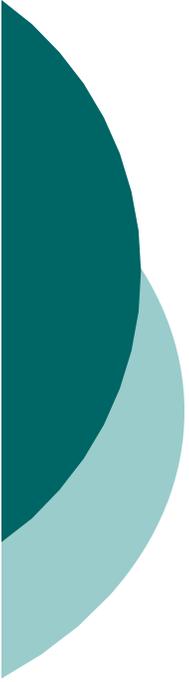
Method 1631E differs from 245.1 in two important aspects.

- ❖ Method 1631E preconcentrates the atomic mercury vapor on a gold trap.
- ❖ Method 1631E uses atomic fluorescence instead of atomic absorption.



Benefits of Method 1631E

- ✓ Allows detection of mercury at 0.5 ng/L; ppt
- ✓ Improved accuracy and precision at low levels
- ✓ Supports measurements at ambient water quality levels
- ✓ Performance based

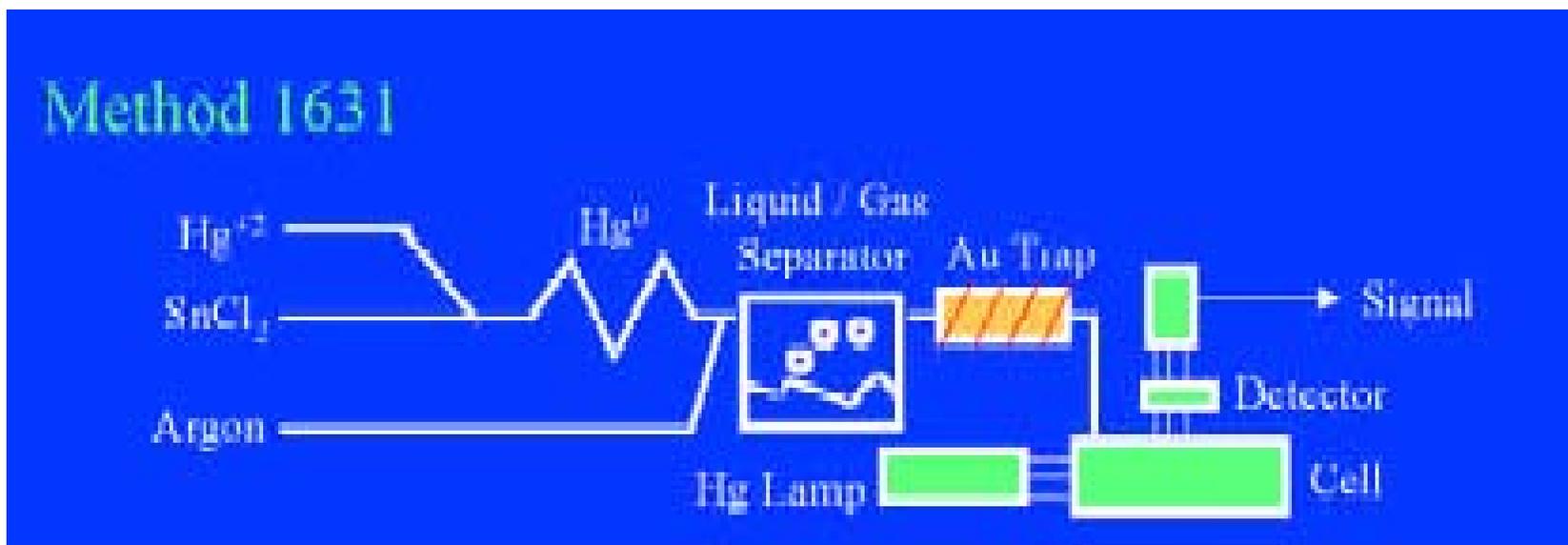


What Does “Performance Based” Mean?

That you may modify the Method provided you demonstrate that your modification achieves performance equivalent or superior to the performance of Method 1631.

THE DIFFERENCE OF FLUORESCENCE

In fluorescence, the light source and detector are placed at right angles to each other so that only light that has been absorbed and reemitted by the analyte reaches the detector.



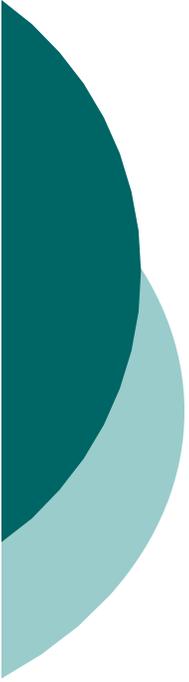
Method 245.1



Method 1631



Figure 1 Method schematics.



ADVANTAGES OF FLUORESCENCE SPECTROMETRY

- The fluorescence technique is generally considered more sensitive
- Has better linearity
- Has a more stable baseline than atomic absorption
- The end result is that, while cold vapor atomic absorption instruments produce detection limits of about 1 ppt.
- Instruments designed for Method 1631E typically produce detection limits on the order of 0.05 ppt.

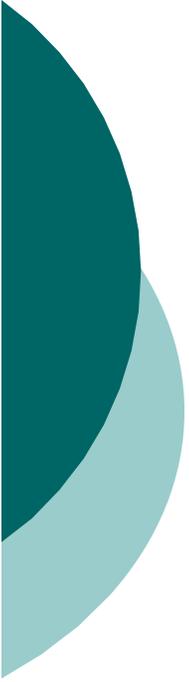


Do I Want to Provide Analysis Using Method 1631?

Documents to consider: (www.epa.gov)

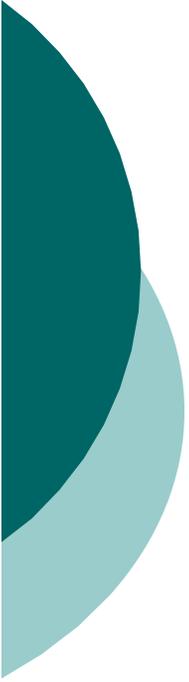
Method 1631, Revision E: *Mercury in water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*, August 2002

- *Guidance for Implementation and Use of EPA Method 1631 for the Determination of Low-Level Mercury* (40 CFR part 136)
- EPA Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, July 1996 (EPA-821-R-96-011)
- *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities*, Draft 1996.
- Video: *Sampling Ambient and Effluent Waters for Trace Metals* (EPA 821-V-97-001)



When Should Method 1631 Be Used?

For compliance monitoring under the National Pollution Discharge Elimination Systems (**NPDES**); ambient water quality monitoring; development of effluent guidelines; and general laboratory use. This rulemaking does not propose to repeal any of the currently approved methods that test for mercury. Each permitting authority must decide which method is appropriate for its needs under EPA's Clean Water Act programs. **(40 CFR part 136)**



Method Considerations

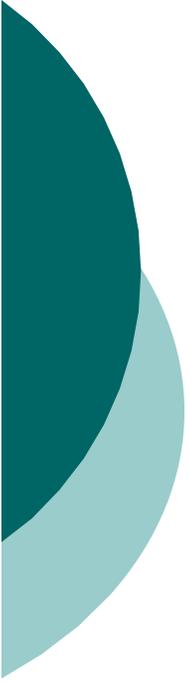
Contamination

- **during sampling** – containers, sampling equipment gloves, reagents
- **transportation**
- **preparation** – reagents, flasks, pipettes, fume hood, and lab air
- **analysis** – auto sampler cups and vials and sample carryover



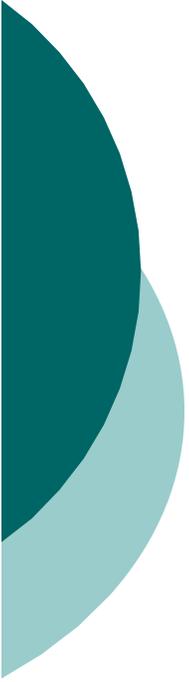
Contamination Control Philosophy

Sampling Guidance (EPA Method 1669): “ The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern.” This means that mercury is eliminated or reduced to a level that will not compromise the measurement. This also applies to the air in the laboratory.



Method Specifics to Generate Acceptable Accuracy and Precision

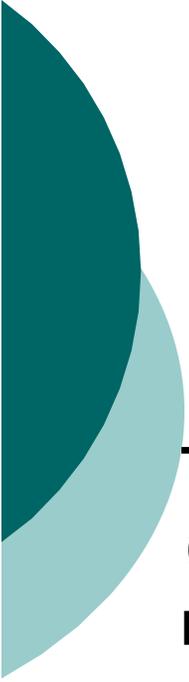
- Class 100 Clean Lab or Class 100 Clean Bench (optional)
- Instrumentation-capable of meeting analytical demands of Method 1631
- Clean Reagents



Method Specifics to Generate Acceptable Accuracy and Precision

Initial Demonstration of Capability

- calibration blank minimum level (**ML**) <0.5 ng/L (mean value of three system blanks)
- relative standard deviation (RSD) <0.1 ng/L for calibration blank
- Calibration Factor precision +/- 15%
- Recovery of lowest standard +/- 25%
- On going precision recoveries +/- 23%
- Method Detection Limit of 0.2 ng/L
- Matrix spike recoveries 71-125 % of true value
- Matrix spike dup relative percent difference +/- 24%
- Method Detection Limit (**MDL**), (40 CFR 136, Appendix B)



Conclusion

The role of EPA Method 1631, Revision E: (Method 1631E), in the determination of mercury (Hg) in water by oxidation, purge and trap, and cold-vapor atomic fluorescence spectrometry, is effective and reliable. However, attention to detail, quality control and the control of sample collection, preparation, and analysis are paramount in providing quality data.